

EFFICIENCIES OF METHANOL PRODUCTION FROM
GAS, COAL, WASTE OR WOOD

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ABSTRACT

In the practical operation of methanol plants using natural gas, an efficiency of 50-65% is achieved, depending on the degree of waste heat recovery. The production of methanol only from coal has an estimated efficiency of 41-55%; but if methane and coal liquids are produced simultaneously, the overall process efficiency can climb to 75%. Waste and wood can also be used as energy sources. Conversion from these sources to methanol is likely to be somewhat less efficient because the plants will be smaller. However, several new processes for gasification and synthesis are being developed which may significantly increase these efficiencies.

The above values are first-law efficiencies measuring the ratio of the combustion energy of the product relative to the input energy. The second-law efficiency, based on free-energy conversion efficiency, is a more fundamental measure of the degree of effectiveness of any process; and it is applied here to several of the steps in methanol manufacture. Data are presented on the free energy of formation, combustion, gasification and reaction for chemical steps of interest in methanol manufacture. The second-law efficiency of methanol manufacture is several percent higher than the first law efficiency.

This work was sponsored by the Methanol Division of the MIT Energy Laboratory.

Introduction

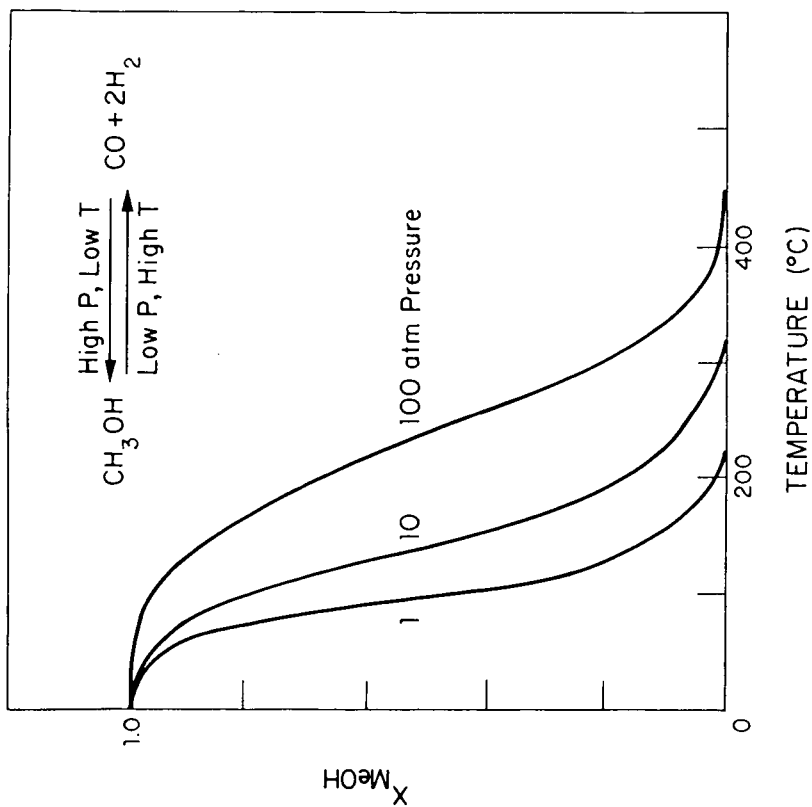
Methanol has become a prime candidate for a clean synthetic liquid fuel to replace our dwindling oil and gas supplies(1-3). It is presently made in the U. S. from natural gas; but it can also be made from coal, waste or wood, and the yield can be greatly increased by using waste heat from a nuclear plant. We discuss in this paper the reported overall energy efficiency of manufacture from these various sources and analyse the energy consumption of the various steps. We will also discuss new methods of estimating efficiency and potential improvements in the various steps.

In practice, methanol plants are built to maximize profits rather than to minimize energy consumption. This may seem to make an analysis of energy consumption academic. Yet the efficiency of each step and the net efficiency must be understood before subsequent technical and economic choices can be made in planning. Now that energy is becoming less plentiful, it is very important that we keep good books on energy consumption.

CHEMICAL SYNTHESIS OF METHANOL

Methanol is generally produced from synthesis gas (syn-gas), a mixture of hydrogen and carbon monoxide, made by partial combustion of organic fuels such as gas, coal or wood. Table I lists the standard free energies of formation of species important in the manufacture of syn-gas and methanol. The available data (4-6) have been fitted to the linear equation $\Delta G = \Delta H - T \Delta S$ where the constants ΔH and ΔS give the best fit to the available data. This greatly simplifies calculations of free energy, equilibrium constants or efficiencies with very little loss of accuracy (6). Data on the free energy of combustion are also presented in Table I. The values for ΔH_c° and ΔG_c° can be used in calculating first and second law efficiencies.

Four routes for methanol synthesis have been considered in the literature, and these are shown in Table II along with the standard free energies of the reactions, where these are available. In practice only the first two routes, catalytic reduction of carbon oxides by hydrogen, are used commercially (7,8). The equilibrium concentration of methanol, x_M , formed in reaction (II-1) is shown in Fig. 1 for various pressures and temperatures. The reaction takes place over a chrome-zinc oxide catalyst at 300 atm between 300 and 400°C (Vulcan Cincinnati and Lurgi Process) or over a copper oxide catalyst at 50-100 atmospheres between 250 and 350°C (ICI Process). Because the reaction is highly exothermic, great care is taken to prevent overheating of the catalyst bed. The excess heat of reaction is usually recovered to make steam to drive the turbine compressors, and indeed some methanol plants generate excess electric power(9).



METHANOL CONVERSION vs TEMPERATURE AND PRESSURE

FIGURE I

Depending on the catalysts used, other alcohols will be produced in, a mixture called "methly-fuel"(10). These improve the fuel value of the methanol, but it is not clear whether the excess hydrogen required can be justified on an energy efficiency basis. The use of iron catalysts and lower pressures can also produce hydrocarbons as well (Fischer-Tropsch Process), but this process has a low energy efficiency because the oxygen in the synthesis-gas is reduced to water by some of the hydrogen(7).

Excess hydrogen is often used to remove heat from the catalyst bed. A new three-phase methanol reactor is being developed by Chem Systems (11,12) in which the gases are dissolved in an oil that fluidizes the catalyst and removes heat. It is reported that 12% of a Lurgi syn-gas or 20% of a Koppers-Totzek (KT) gas were converted to methanol in a single pass at 60 atm and 235°C compared to conversions of 4-5% per pass in present reactors.

Gasification and Gasifiers

Table III lists the principal routes for the manufacture of syn-gas. At present syn-gas is made in the U. S. primarily by the steam reforming of natural gas according to Eqn. (III-3) at 15-20 atm and 850°C. This reaction is highly endothermic and requires a large capital investment in heat exchangers that operate at high pressure and elevated temperatures. The cost of the steam reformer is typically 41% of the total plant cost(13). It can be seen from Eq. (III-3) that an excess of hydrogen is produced and this excess can be used to make ammonia or alternatively, CO₂ can be added to the syn-gas to make more methanol as shown in Eq. (II-2). Methanol is presently made in some countries by the gasification of naphtha, or heavy hydrocarbon residues, according to Eq. (III-5)

Other primary energy sources will have to be found for methanol manufacture as our oil and gas supplies are depleted. Fortunately a wide variety of other feed stocks can be converted to syn-gas and thence to methanol, ammonia, or synthetic gasoline. For example, the water-gas reaction can be used to convert charcoal or coke to the equimolar syn-gas mixture commonly called water-gas. Unfortunately this reaction is highly endothermic, like steam reforming, and requires high-temperature heat exchangers or a revival of early water-gas reactors(7). Carbon can also be gasified with oxygen according to Eq. (III-2), resulting in the production of CO and a great deal of heat. These two reactions can be combined by gasification with a mixture of oxygen and steam in the ratio 0.61 to give an autothermic reaction.

Carbon is not a practical source of energy for syn-gas production. However coal and biomass are both very attractive, and both of these fuels fortunately contain some of the needed hydrogen as shown in Eqns. (III-6,7).

Gasifiers differ in the type of fuel used (coal,

Table I - Standard Free Energy of Formation and Combustion of Species Important in Methanol Manufacture

Substance	$\Delta G_f^{\circ} (T)$ (a) kcal/mole	$\Delta G_c^{\circ} (T)$ (b) kcal/mole
1. $\text{CH}_3\text{OH} (g)$	$-51,500 + 35.5T$	$-159,700 - 10.7T$
2. $\text{CH}_3\text{OH} (l)$	$-59,900 + 60.3T$	$-151,300 - 35.5T$
3. $\text{H}_2\text{O} (g)$	$-58,400 + 12.4T$	0
4. H_2	0	$-58,400 + 12.4T$
5. CO_2	$-94,400 + 0.0T$	0
6. CO	$-26,400 - 21.3T$	$-68,000 + 21.3T$
7. C	0	$-94,400 + 0.0T$
8. CH_4	$-19,600 + 22.1T$	$-191,600 + 2.7T$
9. " CH_2 " (c)	$-3,200 + 22.2T$	$-149,600 - 9.8T$
10. "Coal" (d)	-7,400	-58,900
11. "Wood" (e)	-11,400	-32,200

- (a) The standard free energy of formation from the elements. Data from refs. (4-6) were fitted to a linear equation of the form $\Delta G = \Delta H - T\Delta S$ over the range 300 - 1200 K, so that the two constants in each equation are the effective values of ΔH_f° and $-\Delta S_f^{\circ}$ over this range. Estimated accuracy ± 0.5 kcal. The free energies of combustion and other reactions can be calculated from these values.
- (b) The free energy for the combustion to CO_2 and $\text{H}_2\text{O} (g)$. This is the low free energy of combustion (analogous to the low heating value for the fuel, LHV). The high free energy of combustion is calculated by adding $-9,700 + 26.0T$ to the equation given above for each mole of water in the combustion products.
- (c) The limiting value for paraffinic hydrocarbons, $\text{C}_n\text{H}_{2n+2}$, at high n .
- (d) The natural substances coal and wood have varying properties; the value of ΔH_f° and ΔH_c° given here is for the Clifty Creek No. 6 high-volatile bituminous coal of Ref. 23 used for column 3 of Table 4 in this report. The molecular formula calculated from the ultimate analysis is $\text{C}_{0.54}\text{H}_{0.45}\text{S}_{0.01}\text{N}_{0.01}$.
- (e) For a wood of formula $\text{C}_{0.32}\text{H}_{0.46}\text{O}_{0.22}$, $\Delta G_c^{\circ} = 4.242$ cal/g in "International Critical Tables", Vol. II, p. 131.

Table II

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Standard Free Energies for Methanol Synthesis Reactions

Reaction	$\Delta G_r^0(T)$ kcal/mole
1. $2 \text{ H}_2 + \text{CO} \rightarrow \text{CH}_3\text{OH (g)}$	-25,100 + 56.8T
2. $3 \text{ H}_2 + \text{CO}_2 \rightarrow \text{CH}_3\text{OH (g)} + \text{H}_2\text{O (g)}$	-15,500 + 47.9T
3. $\text{CH}_4 + \text{SO}_3 \rightarrow \text{CH}_3\text{OH} + \text{SO}_2$	-9,300 - 29.2T
4. $\text{CH}_4 + 1/2 \text{ O}_2 \rightarrow \text{CH}_3\text{OH (g)}$	-31,900 + 13.4T
5. $\text{CO} + \text{CH}_3\text{OH} \rightarrow \text{H}_2 + 2 \text{ CH}_3\text{OH}$	-
6. $"\text{CH}_2" + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{OH (g)}$	-10,100 + 0.9T

Table III - Gasification Reactions

Reaction	$\Delta G_r^0(T)$ kcal/mole
1. $\text{C} + \text{H}_2\text{O (g)} \rightarrow \text{CO} + \text{H}_2$	32,000 - 33.7T
2. $\text{C} + 1/2 \text{ O}_2 \rightarrow \text{CO}$	-26,400 - 21.3T
3. $\text{CH}_4 + \text{H}_2\text{O (g)} \rightarrow \text{CO} + 3 \text{ H}_2$	51,600 - 55.8T
4. $\text{CH}_4 + 1/2 \text{ O}_2 \rightarrow \text{CO} + 2 \text{ H}_2$	-6,800 - 43.4T
5. $"\text{CH}_2" + \text{H}_2\text{O} \rightarrow \text{CO} + 2 \text{ H}_2$	35,200 = 55.9T
6. $\text{Coal} + \text{O}_2, \text{H}_2\text{O} \rightarrow \text{CO}, \text{H}_2$	-
7. $\text{Wood} + \text{O}_2, \text{H}_2\text{O} \rightarrow \text{CO}, \text{H}_2$	-
8. $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$	-9,600 + 8.9T

Table IV - Material and Energy Balance for 5000 ton/day

Methanol Production from Coal

Gasifier	Koppers-Totzek	Winkler	Lurgi
Coal	Eastern High Volatile Bit A	Western Sub-bituminous	Western Sub-bituminous
Heat Content BTU/lb	10,690	8640	8870
Consumption - ton/day	8260	11690	20670
Fuel Energy - 10^9 BTU/day	177	202	367
Aux. Energy "	35	35	94
Aux. Coal ton/day	1650	2040	5280
Oxygen ton/day	6700	5000	5500
Methane 10^6 SCF/day	0	0	185
Tars, oils, phenols t/day	0	0	1860
Energy in products 10^9 BTU/d	98	98	344
Process Efficiency %	46	41	75

lignite, waste or wood), in the sizes and amount of fuel they can gasify (0.1-500 tons/day), in the pressure of operation (1-20 atm pressure) and in the method of fuel suspension (fixed bed, suspended particles or fluidized bed). Manufactured gas was in widespread use until pipelines brought natural gas from Texas. Germany and especially Sweden have made synthetic gas and fuels from coal and wood during World War II, so that most of the above combinations of conditions exist or have existed in commercial gasifiers(7,14,15). Oxygen gasifiers typically operate with an efficiency of 65-90% (7), while air gasifiers can be up to 95% efficient.

In addition to many experimental gasifiers under investigation in this country there are three commercially available models that have been in use since World War II: the Lurgi, the Winkler, and the Koppers-Totzek (KT). In methanol production the gasifier is operated as part of a larger process, and the efficiency is not measured independently.

Recently the Union Carbide Corporation has developed an oxygen gasifier for municipal waste under the name Purox. In this system, one ton of waste is gasified with 0.2 tons of oxygen, yielding 0.22 tons of clean, granular residue, 0.7 tons of gas, and 0.28 tons of water. The resulting gas is 26% H_2 , 40% CO , 23% CO_2 and 5% CH_4 , and contains 370 BTU/SCF. Of the 9.5 MMBTU contained in a ton of waste, 7.5 MMBTU are contained in this gas. One million BTU of thermal energy are required to make the oxygen, so that the net energy efficiency of gas production is 68%(16).

Carborundum Corporation has also developed a gasifier for municipal waste that uses preheated air, the Torax gasifier. Battelle has developed an air gasifier for cellulosic wastes that they estimate to be 85% efficient (17). A number of biomass gasifiers are in the development stage (18).

The Thagard Oil Co. has recently announced a reactor capable of operation to 6000°F. It is claimed that carbon-containing feedstocks can be gasified for a fraction of the cost of conventional gasifier operation(19,20).

Gas Preparation

After the raw syn-gas is produced, it must be cleaned of all traces of sulfur, since methanol catalysts are sensitive to sulfur. Then the required hydrogen/carbon-monoxide ratio is established according to the water-gas shift reaction, Eq. (III-8).

Efficiency of Methanol Manufacture

It is customary to define the net energy efficiency of present and projected methanol plants as the ratio of the energy in the products, E_p , to the energy in the fuel and that required to generate auxiliary inputs (such as

electricity and oxygen), E_f and E_a ,

$$\eta = E_p / (E_f + E_a) \quad (1)$$

$$\eta = \Delta H_p^\circ / (\Delta H_f^\circ + \Delta H_a^\circ) \quad (2)$$

The product and fuel energies are usually given as the low heat of combustion of these fuels. These are the ΔH_c° values found in Table I. The auxiliary inputs are given as the thermal equivalent of electric power used. Since large plants produce their own electricity and oxygen, generally from the same fuel (gas, coal, etc.) used to make the methanol, this estimate is both simple to make and reliable. We list here the efficiency of methanol manufacture as reported by various sources.

Natural Gas: R. McGhee (Transco) (13) reports that gas plants have improved their efficiencies from about 25% in the 1930s to 50-60% for modern, large-scale plants. Much of this efficiency increase in plants making more than 200 tons/day of methanol is due to the operation of centrifugal compressors with steam generated from the exothermic heat of reaction (11-1). D. Wentworth of Vulcan-Cincinnati has reported that the high pressure process, leading to methanol containing higher alcohols (Methyl-Fuel), is 63-69% efficient (21). Again it should be stressed that these are not necessarily the maximum attainable efficiencies, but represent an economic compromise in plant construction.

The largest plants presently operating today make 2000 tons/day of methanol, but the largest single-train plant possible to construct with available equipment will make 5000 tons/day of methanol. Plants have been proposed with five trains making 25,000 tons/day of methanol from either natural gas or coal. All the methanol plants in the U. S. today produce together about 10,000 tons/day or a billion gallons/year.

Coal: B. Harney reports a coal-methanol plant operated in Texas in 1955 making 300 tons/day of methanol (22); but this plant was converted to natural gas in 1956, and all plants in the U. S. have since run on natural gas because of its low cost. Recently a number of estimates of costs for large coal-methanol plants have been made. The efficiency of operation must be estimated in order to make these calculations, and a number of these have appeared in print.

During Project Independence, a large group from the AEC interviewed many industrial companies to estimate the cost of making methanol from coal in large plants (23). The estimated plant efficiencies for various methods of gasification of several coals are shown in Table IV, where it can be seen that the efficiency varies between 41 and 75% depending on the production conditions and whether methanol is produced alone or in combination with methane and coal liquids (co-products).

During the gasification of coal, some gasifiers (such as KT and Winkler) produce only CO and H₂. Others, such as

Table V - Efficiency of Manufacture of Synthetic Fuels

Fuel ^(a)	From Shale	Coal Liquefaction	Lurgi
Gasoline	55%	65%	-
Gasoline plus distillate	65	70	-
Methanol	-	-	65%

(a) Does not include energy consumed in producing primary fuel, estimated to be 80-90% efficient for strip mining and 60% efficient for room and pillar shale mining.

(b) Assumes tars, oils from Lurgi gasification used for process heat, otherwise 55% efficient.

Table VI - Efficiency and Cost of SASOL type Synthetic Fuel Production from Coal^(a)

Fuel	Primary Eff. %	Total Eff. %	(b) Costs		(c) Product tons/day
			Plant - \$MM	Product \$/MMBTU	
Methanol	39	56	472	1.80	69
Gasoline	21	41	505	3.05	50
SNG	53	68	365	1.13	78
Low BTU gas	63	71	218	0.86	83

(a) From study Ref. 27.

(b) In 1975 dollars using modified Panhandle Easter accounting, plants burning 20-30,000 tons/day coal

(c) Based on published SASOL technology using Lurgi gasifier

Table VII- Second Law Efficiency of Methanol Production from Methane or Petroleum Feedstocks (Assumed First Law Efficiency 0.60)

	Heat of Combustion	Free Energy of Combustion	First Law Efficiency	Second Law Efficiency
	ΔH_c^0	ΔG_c^0	η	ϵ
CH ₃ OH	-151.3	-161.9		
CH ₄	-191.6	-190.8	0.60	0.64
"CH ₂ "	-149.6	-152.5	0.60	0.63

the Lurgi gasifier, produce sizable quantities of methane and coal chemicals as well. In Table IV it is seen that if these products can be used, the total conversion efficiency is as high as 75%, while much lower efficiencies result for single-product processes.

From data obtained on a Lurgi type gasifier, R. McGhee of Transco projects a conversion efficiency of 54% for the production of methane alone. If the methane produced naturally in gasification is used as is and if the balance of the coal is converted to methanol, the overall efficiency is projected to be 52%. If the coal-tar liquids can be used as well, the efficiency increases to 61%(24).

In a recent study for the EPA, the EXXON staff estimated the efficiency of production of synthetic gasoline, distillate, and methanol from shale and coal. Their results are shown in Table V. The efficiencies for methanol production are based on established technology, while production from shale and coal liquifaction are in the development stage. The efficiencies of production of the primary fuels were also estimated in this report as 60% for room and pillar shale mining and 80-90% for coal mining(25).

In Germany in 1938, 58% of the motor fuel was synthetic, manufactured from coal, wood, and agricultural products(26). About half of this production was gasoline made from brown coal with the Fischer-Tropsch synthesis. This technology was transferred after the war to the SASOL Corporation in South Africa where it is now being greatly expanded. In a recent study, F. K. Chan of Kellogg Corp. has used published SASOL data to estimate the efficiencies and costs of making various synthetic fuels (27). His results are shown in Table VI. Since the SASOL process uses Lurgi gasification, the efficiency is high only when coproducts are produced.

The manufacture and use of methanol as a fuel has been examined in considerable detail in a recent study (28) by the West German Government. It projects a requirement of 1.46 tons of hard coal, 5.37 tons of lignite, or 1120 cubic meters of natural gas per ton of methanol synthesized. These figures correspond to thermal efficiencies of 46% for coal and lignite and 55% for natural gas. The fuel requirement can be greatly reduced if the plant is coupled to a nuclear plant for process heat.

Waste and Wood: The possible manufacture of methanol from municipal waste is a potentially attractive solution for both our waste disposal and energy shortage problems. The City of Seattle has explored various disposal schemes and finds that the manufacture of methanol or ammonia, depending on market conditions, offers the most economical method of waste disposal, even though it also requires the largest amount of capital (29). In a study for the City it is estimated that 1500 tons/day of waste can produce 1000 tons/day of synthesis-gas which in turn will produce 275 tons/day of methanol at a cost of 19,000 kwh of electric

power. The net energy efficiency estimated from these inputs is about 34% (30). Methanol has never been made from waste or wood, but no problems are apparent in doing so, since these fuels can be gasified to syn-gas. In fact cellulosic type fuels have typically less than 0.1% sulfur whereas coal has 2% or more. Methanol catalysts are particularly sensitive to sulfur, so this is an advantage. The efficiencies of conversion should be comparable, on an energy basis, to those predicted above for coal. It is estimated that 1 ton of methanol (17 MMBTU/ton) can be made from 3 tons of dry wood (16 MMBTU/ton) or 5.1 tons of waste (typically containing 9 MMBTU/ton) based on a conversion efficiency of 37%. However efficiencies could be significantly higher or lower depending on plant size and degree of heat recovery (31).

Second Law Efficiencies

So far we have been discussing what can be called a first law efficiency of methanol conversion, gasification, etc. which is defined in Eq. (1) as the ratio of the energy content of the products to the energy inputs. This criterion can be misleading. It is possible to convert between chemical, electrical and mechanical energy with an efficiency approaching 100%. However we cannot convert thermal energy to the other forms without losing a fraction $(T_2 - T_1)/T_2$ when we use a heat engine. In converting other energy forms to thermal energy, we can gain the fraction $T_1/(T_2 - T_1)$ by using a heat pump. These relations are illustrated in Fig. 2.

The second law efficiency has been defined (32-35) as

$$\epsilon = \frac{(\text{heat or work usefully transferred by a device})}{(\text{maximum heat or work transferrable by any device})} \quad (3)$$

In examining chemical processes, the change in Gibbs free energy, ΔG , accompanying a chemical process is the proper measure of chemical energy consumed or produced in that reaction and determines the maximum efficiency of the production of chemical, electrical or mechanical energy.

For the conversion of primary fuels to synthetic fuels, we define the second law efficiency as the ratio of the free energies of combustion (at 300K) of the products to those of the inputs,

$$\epsilon = \Delta G_c^\circ(\text{products})/\Delta G_c^\circ(\text{fuel}) \quad (4)$$

(where ΔG_c° is the free energy of combustion of the primary fuel, whether it is used as a feedstock or for auxiliary energy production.)

The values of ΔH_c° and ΔG_c° at 300K are shown in Table VII for methanol and several primary fuels. It can be seen that the free energy of combustion of methanol is significantly higher than the heat of combustion, while for

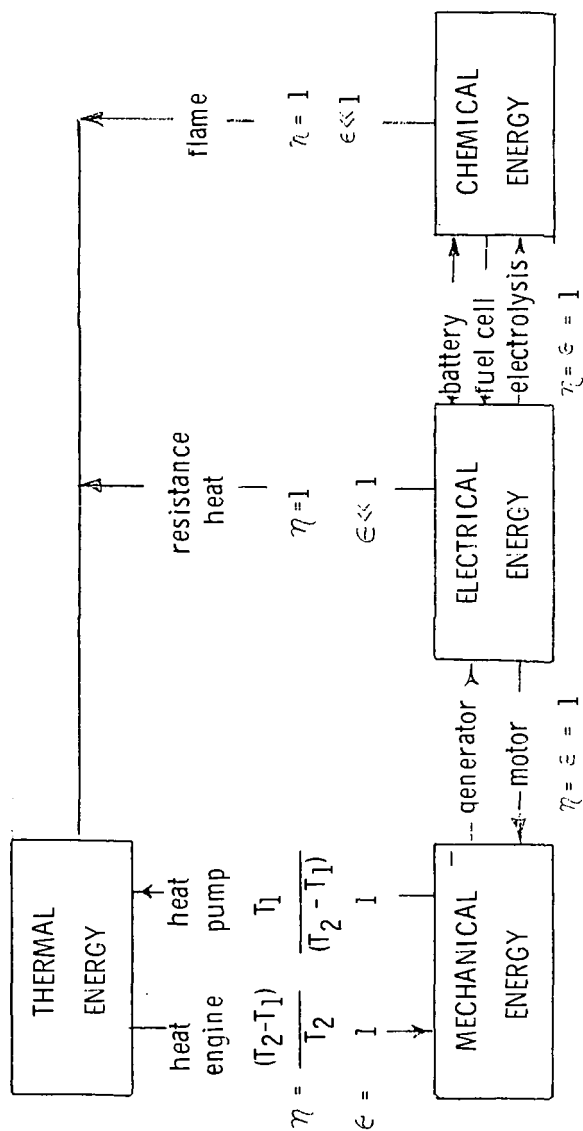


Fig. 2 - Maximum first and second law efficiencies for various energy conversions

FIGURE 2

the primary fuels, these quantities are approximately equal. The overall second law efficiency of methanol production from methane or petroleum is compared to an assumed first law efficiency of 0.60 in Table VII. The second law efficiency is several percent higher and this is due to the large entropy term in the free energy of combustion of methanol.

The formation of methanol is highly exothermic (Eqs. 11-1,2,4,6) which would at first suggest that a great deal of energy is lost in conversion from other fuels. It is precisely because the heats of combustion do not determine efficiencies that in fact practical synthesis of methanol is relatively efficient. Although a great deal of heat is produced at various stages in processing, this heat can be recovered as work for compression and appears in the methanol as recovered free energy.

Although the use of second law efficiencies does not greatly change the overall conversion efficiency in methanol production, it gives much more insight into the separate steps of production and points up the areas where improvements can be made. A few examples will make this clearer.

Since gasification of feedstocks generally leads to a ratio, $R = H_2/CO$ different from that of 2 required for methanol synthesis, it is necessary to perform the watergas shift reaction, Eq. (III-8) on the raw syn-gas, and this reaction consumes a quantity of free energy calculated as follows. The free energy of any reacting mixture is given by (36)

$$G = n_i \sum \mu_i \quad (5)$$

where

$$\mu_i = \mu_i^\circ + RT \ln X_i \quad (6)$$

(Here μ_i is the chemical potential of each species, n_i is the number of moles of each species in the mixture, and X_i is the mole fraction of each species. If we take $x = H_2/CO$, as a measure of the degree of reaction, Eq. (5) becomes

$$G(x) - (G_{CO} + G_{H_2O}) = x \Delta G_R^\circ + RT \ln P + 2RT (x \ln x + (1-x) \ln(1-x)) \quad (7)$$

This free energy loss on reaction is shown as a function of the degree of reaction in Fig. 2 for a total pressure of 1 atm at 500K and 1000K. Note that even for $x = 0$ there is a change from the standard free energy of the reactants due to the initial mixing of the reactants. Then as the reaction proceeds, there is a further decrease in free energy due to both enthalpy production and further mixing of the product gases. The free energy reaches a minimum at a value x determined by the equilibrium constant.

From this graph it is possible to calculate the free energy cost of going from any initial ratio R to the value

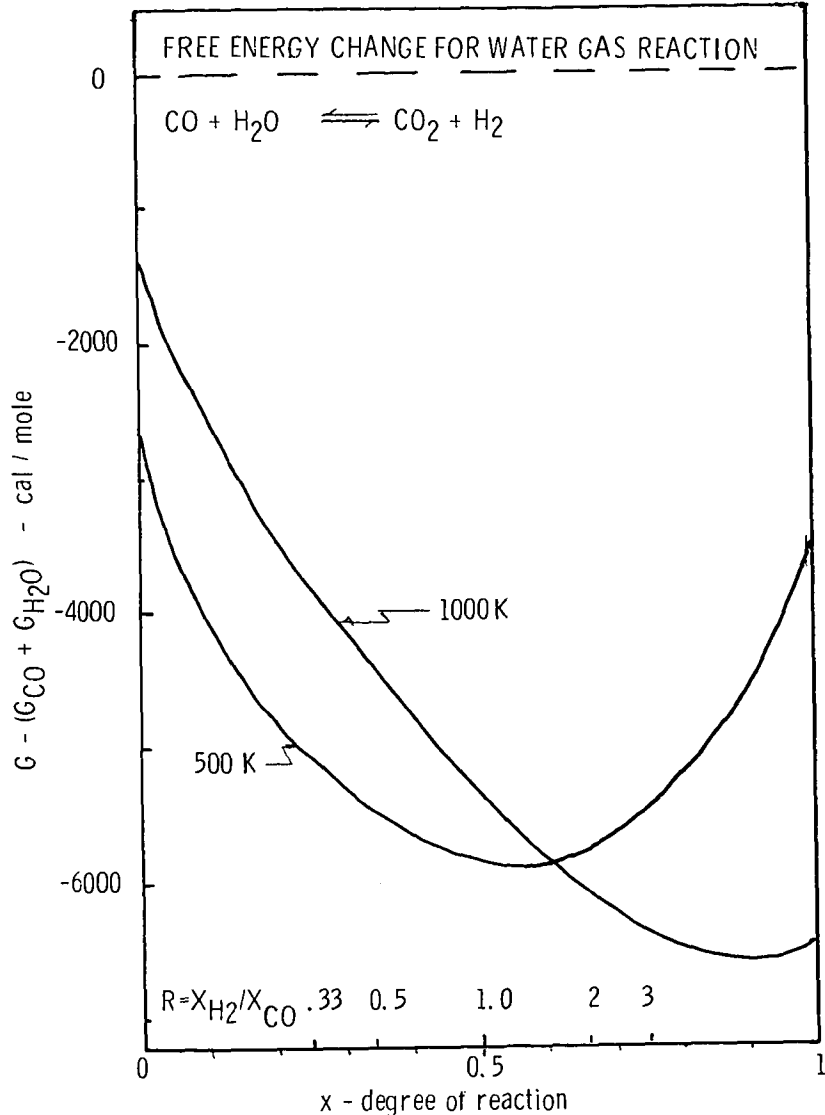
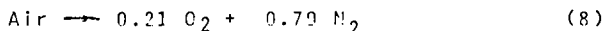


Fig. 3

FIGURE 3

$R=2$ required for methanol synthesis. For instance, starting with $R = 1$, the free energy decreases from -5300 to -6100 or about -800 cal per mole of mixture (-2400 cal/mole of syn-gas, $R = 2$) at 1000K.

Oxygen is often used for the gasification reactions of Table III. The first law gives no value for the efficiency of separation of oxygen from air, since the heat content of the separated O and N is the same as that before separation. For the reaction



the free energy change from Eq. (5) is given by

$$\Delta G = RT (0.21 \ln 0.21 + 0.79 \ln 0.79) \quad (9)$$

This can be easily compared to the electrical or thermal energies required to operate an oxygen plant. According to one manufacturer, 240 kwh are required to produce a ton of oxygen, while from Eq. (8) we calculate a minimum requirement at 300K of 48.1 kwh/ton, yielding an efficiency of 20%. (This converts to 7% thermal efficiency if one assumes an efficiency of 33% for power generation). Gyftopoulos et al (36) derive a second law efficiency of 17% for an oxygen plant making 380 tons/day of oxygen. efficiency of the process.

It is hoped that this brief discussion will encourage the use of second law efficiencies to analyse the various steps in methanol manufacture in second law terms to determine where improvements can be made using new processes and devices such as heat pumps and fuel cells now being developed.

ACKNOWLEDGEMENTS

We are glad to acknowledge the generous support of the Methanol Division by Mr. J. W. Hawley Jr.

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